

Pair correlation functions in nematics, free-energy functional and isotropic-nematic transition

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(Dated: February 6, 2008)

Abstract

We develop a free energy functional for an inhomogeneous system that contains both symmetry conserved and symmetry broken parts of the direct pair correlation function. These correlation functions are found by solving the Ornstein-Zernike equation with the Percus-Yevick closure relation. The method developed here gives the pair correlation functions in the ordered phase with features that agree well with the results found by computer simulations. The theory predicts accurately the isotropic-nematic transition in a system of anisotropic molecules and can easily be extended to study other ordered phases such as smectics and crystalline solids.

PACS numbers: 64.70.Md, 64.70.Dv, 05.70.Ce

The freezing of a fluid of anisotropic molecules into a uniaxial nematic phase is a typical example of a first-order phase transition in which the continuous symmetry of the isotropic phase is broken[1]. In a nematic phase, molecules are aligned along a particular but arbitrary direction so as to have a long range order in orientation while the translational degrees of freedom remain disordered as in the isotropic fluid. At the isotropic-nematic transition the isotropy of the space is spontaneously broken and, as a consequence, the correlations in the distribution of molecules loose their rotational invariance. By computer simulations of a system of ellipsoids Phoung and Schmid [2] have recently evaluated the effect of breaking of rotational symmetry on pair correlation functions (PCFs) and showed that in the nematic phase there are two qualitatively different contributions : one that preserves rotational invariance and other that breaks it and vanishes in the isotropic phase. The symmetry preserving part of the PCFs passes smoothly without any abrupt change through the isotropic-nematic transition. This we expect to be true in most of the symmetry breaking first-order transitions.

The correlation functions that describe the distribution of molecules in a classical fluid can be given as the simultaneous solution of an integral equation, the Ornstein Zernike (OZ) equation, and an algebraic closure relation that relates correlation functions to the pair potential. Well known approximations to the closure relation are the Percus-Yevick (PY) relation, the hypernetted-chain (HNC) relation and the mean spherical approximation (MSA)[3]. This approach has been used quite successfully to describe the structure of isotropic fluids. However, the application of the theory to ordered phases which can be regarded as an inhomogeneous "fluid", has so far been very limited though no features of the theory inherently prevent it from being used to describe structures of the ordered phases like crystalline solids, liquid crystals, etc. Holovko and Sokolovska [4] have used the MSA and Lovett equation[5] which relates one-particle density to the PCFs to solve analytically the OZ equation for a model of spherical particles with the long range anisotropic interaction and determined the PCFs in the nematic phase. However, when Phoung and Schmid[2] used the PY closure relation and the Lovett equation and solved the OZ equation numerically for system of soft ellipsoids nematic phase was not found and for this the PY closure was blamed. Here we adopt a method based on density-functional formalism and show that though the PY relation may not be very accurate it, however, leads to nematic phase with PCFs harmonic coefficients having features similar to those found by simulations[2] and by

analytical solution[4].

A density-functional theory (DFT) of freezing transition requires an expression of the grand thermodynamic potential of the system in terms of one- and two particle distribution functions and a relation that relates the one-particle density distribution $\rho(\mathbf{x})$ to the PCFs. Such a relation is found by minimizing the grand thermodynamic potential with respect to $\rho(\mathbf{x})$ with appropriate constraints[6]. The correlation functions that appear in these equations are of the ordered phase and are functional of $\rho(\mathbf{x})$. The free energy functional that exist in the literature[7, 8] and have been used to study the freezing transitions and other properties of the ordered phases replace these correlations by that of the isotropic fluids (see ref.[6] for details). This approximation limits the applicability of the theory and needs improvement.

Though in this letter we consider the nematic phase, the method developed here is equally applicable to other phases such as smectics and crystalline solids. We first show how the fact that the PCFs in the ordered phase have two distinct parts, leads us to divide the OZ equation and the closure relation into two sets of equations. The solutions of these equations give us both the symmetry conserving and symmetry breaking parts of the PCFs. Using these correlation functions we construct a free energy functional. This free energy functional is then used to calculate the transition parameters of the isotropic-nematic transition in a model system of elongated rigid molecules interacting via the Gay-Berne (GB) pair potential[9]. The GB potential between a pair of molecules (i, j) is written as

$$u(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j) = 4\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j)(R^{-12} - R^{-6}) \quad (1)$$

where $R = (r_{ij} - \sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j) + \sigma_0)/\sigma_0$ and $\hat{\mathbf{e}}_i$ is the unit vector specifying the axis of symmetry of the i th molecule. The expressions for the angle dependent range parameter σ and potential well depth function ϵ contain four parameters x_0, k', μ and ν . These parameters measure the anisotropy in the repulsive and attractive forces. The distance and energy are scaled by parameters σ_0 and ϵ_0 , respectively. The values of the parameters x_0, k', μ and ν are taken 3.0, 5.0, 2.0 and 1.0 respectively. This model system is found to exhibit first-order isotropic-nematic transition[10].

The OZ equation which relates the total PCF, $h(\mathbf{x}_1, \mathbf{x}_2)$, with DPCF, $c(\mathbf{x}_1, \mathbf{x}_2)$, in an inhomogeneous system is written as [6,11]

$$h(\mathbf{x}_1, \mathbf{x}_2) = c(\mathbf{x}_1, \mathbf{x}_2) + \int c(\mathbf{x}_1, \mathbf{x}_3)\rho(\mathbf{x}_3)h(\mathbf{x}_3, \mathbf{x}_2)d\mathbf{x}_3 \quad (2)$$

where \mathbf{x}_i indicates both position \mathbf{r}_i and orientation $\boldsymbol{\Omega}_i$ of the i th molecule, $d\mathbf{x}_3 = d\mathbf{r}_3 d\boldsymbol{\Omega}_3$ and $\rho(\mathbf{x}_3)$ is the single particle density distribution. The PY relation is expressed as

$$c(\mathbf{x}_1, \mathbf{x}_2) = (e(\mathbf{x}_1, \mathbf{x}_2) - 1)[1 + h(\mathbf{x}_1, \mathbf{x}_2) - c(\mathbf{x}_1, \mathbf{x}_2)] \quad (3)$$

where $e(\mathbf{x}_1, \mathbf{x}_2) = \exp[-\beta \mathbf{u}(\mathbf{x}_1, \mathbf{x}_2)]$. The pair correlation functions h and c are assumed to be sum of two parts; one which corresponds to rotationally invariant and other which corresponds to the breaking of the rotational symmetry. Thus

$$h = h^{(0)} + h^{(n)} \quad \text{and} \quad c = c^{(0)} + c^{(n)} \quad (4)$$

This allows us to write the OZ and PY equations as

$$\begin{aligned} h^{(0)}(\mathbf{x}_1, \mathbf{x}_2) &= c^{(0)}(\mathbf{x}_1, \mathbf{x}_2) + \rho_0 \int c^{(0)}(\mathbf{x}_1, \mathbf{x}_3) \\ &\quad \times h^{(0)}(\mathbf{x}_3, \mathbf{x}_2) d\mathbf{x}_3 \end{aligned} \quad (5)$$

$$\begin{aligned} c^{(0)}(\mathbf{x}_1, \mathbf{x}_2) &= (e(\mathbf{x}_1, \mathbf{x}_2) - 1)[1 + h^{(0)}(\mathbf{x}_1, \mathbf{x}_2) - \\ &\quad c^{(0)}(\mathbf{x}_1, \mathbf{x}_2)] \end{aligned} \quad (6)$$

and

$$\begin{aligned} h^{(n)}(\mathbf{x}_1, \mathbf{x}_2) &= c^{(n)}(\mathbf{x}_1, \mathbf{x}_2) \\ &\quad + \int c^{(0)}(\mathbf{x}_1, \mathbf{x}_3) \rho_n(\mathbf{x}_3) h^{(0)}(\mathbf{x}_3, \mathbf{x}_2) d\mathbf{x}_3 \\ &\quad + \int (\rho_0 + \rho_n(\mathbf{x}_3)) [c^{(0)}(\mathbf{x}_1, \mathbf{x}_3) h^{(n)}(\mathbf{x}_3, \mathbf{x}_2) \\ &\quad + c^{(n)}(\mathbf{x}_1, \mathbf{x}_3) h^{(0)}(\mathbf{x}_3, \mathbf{x}_2) \\ &\quad + c^{(n)}(\mathbf{x}_1, \mathbf{x}_3) h^{(n)}(\mathbf{x}_3, \mathbf{x}_2)] d\mathbf{x}_3 \end{aligned} \quad (7)$$

$$\begin{aligned} c^{(n)}(\mathbf{x}_1, \mathbf{x}_2) &= (e(\mathbf{x}_1, \mathbf{x}_2) - 1)[h^{(n)}(\mathbf{x}_1, \mathbf{x}_2) - \\ &\quad c^{(n)}(\mathbf{x}_1, \mathbf{x}_2)] \end{aligned} \quad (8)$$

Here $\rho(\mathbf{x}_3) = (\rho_0 + \rho_n(\mathbf{x}_3))$ where ρ_0 is the bulk number density and $\rho_n(\mathbf{x}_3) = \rho_0(f(\boldsymbol{\Omega}_3) - 1)$. $f(\boldsymbol{\Omega})$ is the single particle orientation distribution function normalized to unity, i.e. $\int f(\boldsymbol{\Omega}) d(\boldsymbol{\Omega}) = 1$.

Eqs(5) and (6) give relations that are identical to the one used in calculating the PCFs in an isotropic phase. Relations given by (7) and (8) are new and as shown below give PCFs arising due to breaking of symmetry. To solve these equations we chose a coordinate

frame where the z-axis points in the direction of director \hat{n} (director frame). All orientation dependent functions are expanded in spherical harmonics $Y_{lm}(\Omega)$ [2,12]. This yields (for uniaxial nematic phase of axially symmetric molecules)

$$f(\Omega) = \frac{1}{\sqrt{4\pi}} \sum_{l(\text{even})} f_l Y_{l0}(\Omega) \quad (9)$$

and

$$\begin{aligned} \psi(r, \Omega_1, \Omega_2) = & \sum_{l_1 l_2 l m_1 m_2 m} \psi_{l_1 l_2 l m_1 m_2 m}(r) Y_{l_1 m_1}(\Omega_1) \\ & Y_{l_2 m_2}(\Omega_2) Y_{lm}^*(\hat{r}) \end{aligned} \quad (10)$$

where $f_l = \sqrt{(2l+1)} P_l$ and ψ stands for h, c or e . P_l is the order parameter; its value is zero in the isotropic phase and non-zero in the nematic phase. In uniaxial symmetric phases, only real coefficients with $m_1 + m_2 - m = 0$ and even $l_1 + l_2 + l$ enter the expansion. Since the molecules in the model system under consideration have axial symmetry, every single l is even as well. Because $h^{(0)}, c^{(0)}$ and e preserve the rotational symmetry, for them

$$\psi_{l_1 l_2 l m_1 m_2 m}(r) = \psi_{l_1 l_2 l}(r) C_g(l_1 l_2 l m_1 m_2 m) \quad (11)$$

where C_g is the Clebsch-Gordan coefficient.

We have solved (5) and (6) for the model system of (1) using a method described in ref.[13] and determined the values of $c_{l_1 l_2 l m_1 m_2 m}^{(0)}(r)$ and $h_{l_1 l_2 l m_1 m_2 m}^{(0)}(r)$ for values of l, l_i up to $l_{max} = 8$ at reduced temperature $T^*(\equiv k_B T/\epsilon_0) = 1.0$ and for densities $0 \leq \rho^*(\equiv \rho \sigma_0^3) \leq 0.36$.

To solve (7)-(8) we first set up linear equations for $h_{l_1 l_2 l m_1 m_2 m}^{(n)}(r)$ and $c_{l_1 l_2 l m_1 m_2 m}^{(n)}(r)$ using the expansions of eqn.(9) and (10). In these equations $h_{l_1 l_2 l m_1 m_2 m}^{(0)}(r)$, $c_{l_1 l_2 l m_1 m_2 m}^{(0)}(r)$ and the order parameters P_l appear. Here we restrict ourselves to only one order parameter P_2 and solve these equations for $0 \leq P_2 \leq 0.70$ at the interval of $\Delta P_2 = 0.05$ for all densities between 0 and 0.34 and for l, l_i up to $l_{max} = 4$. Though we followed the same iterative method as used in the case of isotropic, but examined the behavior of each harmonic coefficients $h_{l_1 l_2 l m_1 m_2 m}^{(n)}$ at large distance and ensured that the proper convergence takes place (the computational details will be given elsewhere[14]). The PCFs thus generated are used in constructing the free energy functional.

The reduced free energy $A[\rho]$ of an inhomogeneous system is a functional of density $\rho(\mathbf{x})$ and is written as [6]

$$A[\rho] = A_{id}[\rho] + A_{ex}[\rho] \quad (12)$$

The ideal gas part $A_{id}[\rho]$ is exactly known,

$$A_{id}[\rho] = \int d\mathbf{x} \rho(\mathbf{x}) [\ln\{\rho(\mathbf{x})\Lambda\} - 1] \quad (13)$$

where Λ is the cube of the thermal wavelength associated with a molecule. The excess part arising due to intermolecular interaction is related with the DPCF of the system as

$$\begin{aligned} \frac{\delta^2 A_{ex}}{\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)} &= -c(\mathbf{x}_1, \mathbf{x}_2; [\rho]) \\ &= -c^{(0)}(\mathbf{x}_1, \mathbf{x}_2; \rho_0) \\ &\quad -c^{(n)}(\mathbf{x}_1, \mathbf{x}_2; [\rho]) \end{aligned} \quad (14)$$

$A_{ex}[\rho]$ is found by functional integration of (14). In this integration the system is taken from some initial density to the final density $\rho(\mathbf{x})$ along a path in the density space, the result is independent of the path of the integration[15]. For the symmetry conserving part $c^{(0)}$ the integration in density space is done taking isotropic fluid of density ρ_l (the density of coexistence fluid) as reference. This leads to

$$\begin{aligned} A_{ex}^{(0)}[\rho] &= A_{ex}(\rho_l) - \frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \Delta\rho(\mathbf{x}_1) \Delta\rho(\mathbf{x}_2) \\ &\quad \times \bar{c}(\mathbf{x}_1, \mathbf{x}_2) \end{aligned} \quad (15)$$

where

$$\bar{c}(\mathbf{x}_1, \mathbf{x}_2) = 2 \int d\lambda \lambda \int d\lambda' c^{(0)}\{\mathbf{x}_1, \mathbf{x}_2; \rho_l + \lambda\lambda'(\rho_0 - \rho_l)\}$$

$\Delta\rho(\mathbf{x}) = \rho(\mathbf{x}) - \rho_l$, $A_{ex}(\rho_l)$ is the excess reduced free energy of the isotropic fluid of density ρ_l and ρ_0 is the average density of the ordered phase.

In order to integrate over $c^{(n)}[\rho]$, we characterize the density space by two parameters λ and ξ which vary from 0 to 1. The parameter λ raises density from 0 to ρ_0 as it varies from 0 to 1 whereas parameter ξ raises the order parameter from 0 to P_2 as it varies from 0 to 1. This integration gives

$$A_{ex}^n[\rho] = -\frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \tilde{c}(\mathbf{x}_1, \mathbf{x}_2) \quad (16)$$

where

$$\begin{aligned} \tilde{c}(\mathbf{x}_1, \mathbf{x}_2) &= 4 \int_0^1 d\xi \xi \int_0^1 d\xi' \int_0^1 d\lambda \lambda \int_0^1 d\lambda' \\ &\quad \times c^{(n)}(\mathbf{x}_1, \mathbf{x}_2, \lambda\lambda' \rho_0; \xi\xi' P_2) \end{aligned}$$

It is important to note that while integrating over λ the order parameter P_2 is kept fixed and while integrating over ξ the density is kept fixed. The result does not depend whether integration is done first over λ or ξ . The free energy functional of an ordered phase is the sum of (13), (15) and (16). Note that the Ramakrishnan and Yousuff (RY) [7] free energy functional is the sum of only (13) and (15) and contains an additional approximation in which $\bar{c}(\mathbf{x}_1, \mathbf{x}_2)$ in (15) is replaced by $c(\mathbf{x}_1, \mathbf{x}_2; \rho_l)$.

The grand thermodynamic potential defined as $-W = A - \beta\mu \int d\mathbf{x}\rho(\mathbf{x})$ where μ is the chemical potential, is preferred to locate the freezing transition as it ensures the pressure and chemical potential of the two phases remain equal at the transition. The transition point is determined by the condition $\Delta W = W_l - W = 0$. The order parameters are determined from equations found by minimizing the grand thermodynamic potential with appropriate constraints [6, 14]. The isotropic-nematic transition at $T^* = 1.0$ with one order parameter is found to take place at $\rho_l^*(= \rho_l\sigma_0^3) = 0.3325$ with change in density $\Delta\rho^*(\equiv (\rho_o - \rho_l)/\rho_l) = 0.0086$ and order parameter $P_2 = 0.40$. If one uses the RY free energy functional then the transition takes place at $\rho_l^* = 0.3570$ with $\Delta\rho^* = 0.0055$ and $P_2 = 0.439$. The symmetry breaking part of PCFs makes the isotropic phase unstable and induces the emergence of the ordered phase at lower density.

In Figs 1 and 2 we show some harmonic coefficients of DPCF in the director space for $T^* = 1.0, \rho^* = 0.3361$ and $P_2 = 0.44$. While the harmonic coefficient $c_{220000}(r^*)$ and $c_{2201-10}(r^*)$ shown in Fig 1 survive both in the isotropic ($P_2 = 0$) and the nematic phases($P_2 \neq 0$), the harmonic coefficients $c_{200000}(r^*)$ and $c_{002000}(r^*)$ survive only in the nematic phase and vanish in the isotropic phase. The contribution arising due to symmetry breaking to the harmonic coefficients $c_{220000}(r^*)$ and $c_{2201-10}(r^*)$ are shown by dot-dashed line in Fig 1 and are found to be small compared to the symmetry conserving part. Few selected harmonic coefficients of h are shown in Figs 3 and 4 in director space. In Fig 3 we plot the harmonic coefficients $h_{200000}(r^*)$ and $h_{002000}(r^*)$ which survive only in the nematic phase and note the oscillatory behavior which continues to survive for large values of the intermolecular separation $r^*(\equiv r/\sigma_0)$. In Fig 4 we plot harmonic coefficient $h_{2201-10}(r^*)$ which is of fundamental importance and defines nematic elastic constants[1]. As shown in the figure it decays as $1/r^*$ at large distance. This long-range tail behaviour is attributed to the director transverse fluctuations[4]. This behaviour has been shown analytically by Holovko and Sokolovska[4] and by computer simulation by Phoung and Schmid[2].

The density functional approach allows one to include more order parameters in the theory even though they are not included in calculating the PCFs. This is done through the parametrization of $\rho(\mathbf{x})$ (see [6]). When we take two order parameters P_2 and P_4 and use the free energy functional developed here the transition is found to take place at $T^* = 1$ with $\rho_l^* = 0.317$, $\Delta\rho^* = 0.026$, $P_2 = 0.644$ and $P_4 = 0.332$. These values compare well with the computer simulation values, $\rho_l^* = 0.32$, $P_2 = 0.66$ and $P_4 = 0.29$ [10]. This comparison suggests that the effect of order parameter P_4 on the PCFs is small. However, this does not mean that those harmonics that do not appear in the free energy functional are not sensitive to the values of P_4 . Inclusion of higher order parameters in calculation of PCFs is straightforward though computationally demanding.

In conclusion; we developed a method of solving the OZ equation with a closure relation to get both the symmetry conserving and symmetry breaking parts of PCFs. Using these correlation functions we constructed a free energy functional to study the freezing transition and other properties of the ordered phase. Since the symmetry breaking parts of PCFs have features of the ordered phase including its geometrical packing, the free energy functional proposed here will allow us to study various phenomena of the ordered phases including their relative stability[14]. Lastly we would like to emphasize that the theory developed here can easily be extended to study other ordered phases such as smectics and crystalline solids.

We thank J. Ram for his help in computation. This work was supported by a research grant from DST of Govt. of India, New Delhi.

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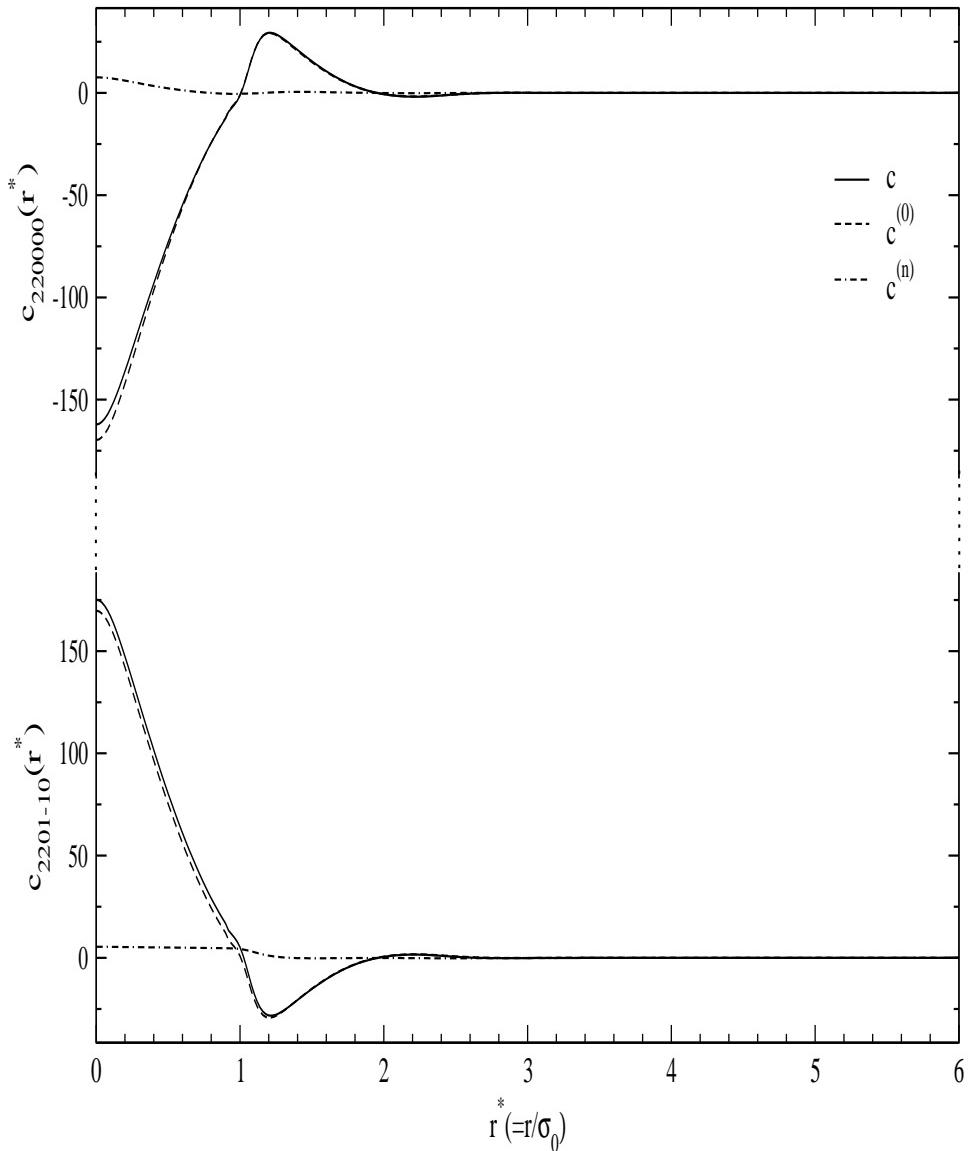


FIG. 1: Harmonic coefficients of the DPCF in the director frame at $\rho^* = 0.3361$, $T^* = 1.0$ and $P_2 = 0.44$. The dashed line shows the contribution arising due to symmetry conserving part, dot-dashed line the symmetry broken part and the full line the resultant.

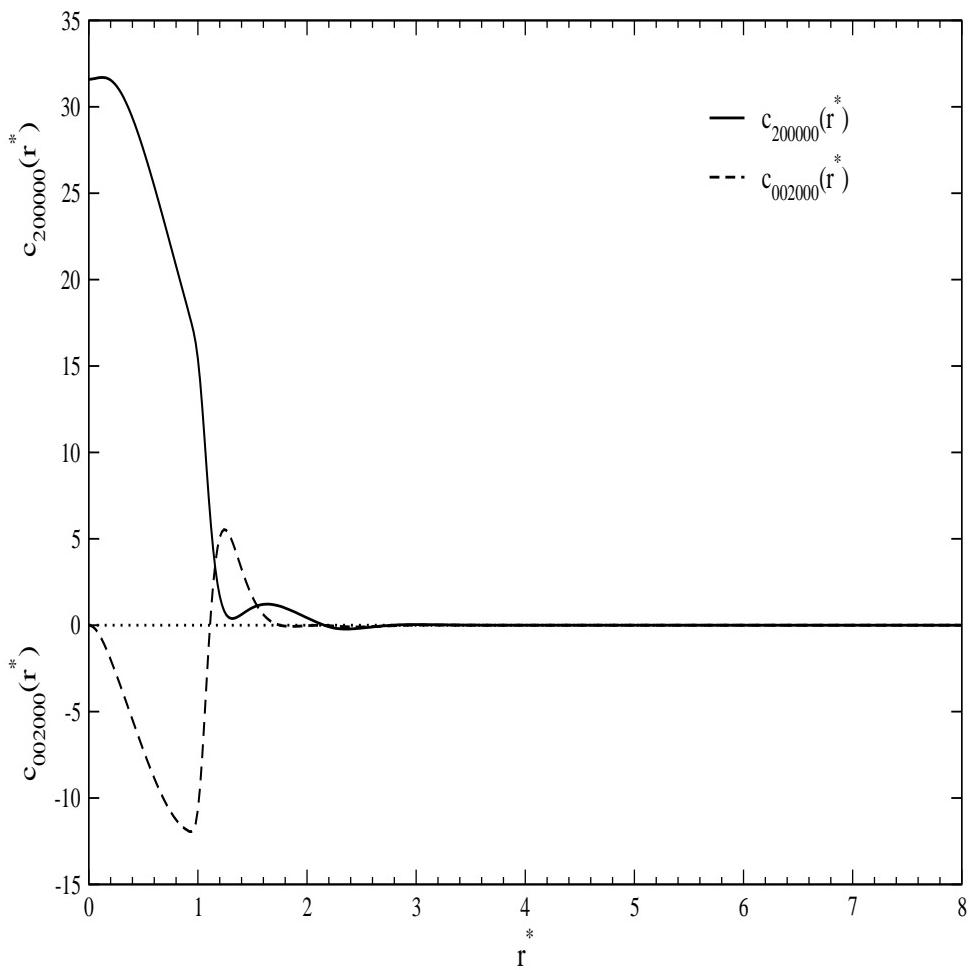


FIG. 2: Harmonic coefficients of the DPCF in the director frame at $\rho^* = 0.3361$, $T^* = 1.0$ and $P_2 = 0.44$. The contributions to these coefficients arise due to the symmetry breaking part only.

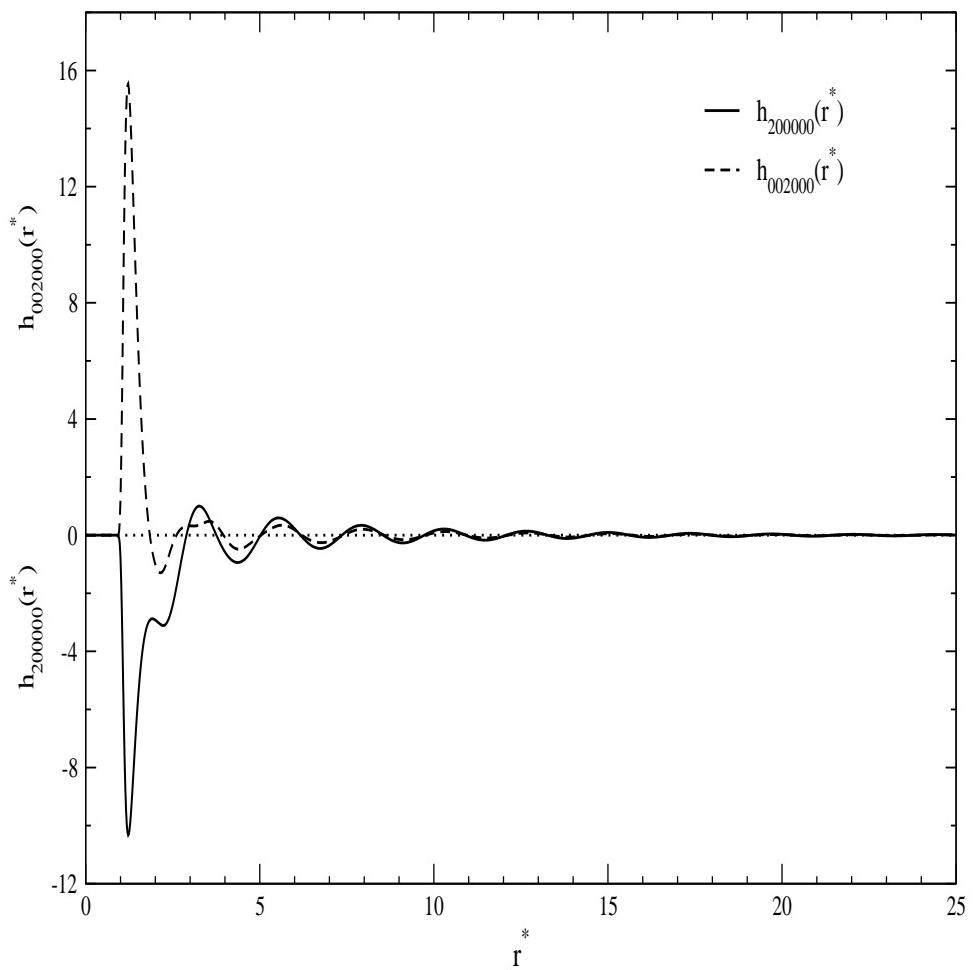


FIG. 3: Symmetry breaking h-harmonic coefficients in the director frame. Details are same as in Fig 2.

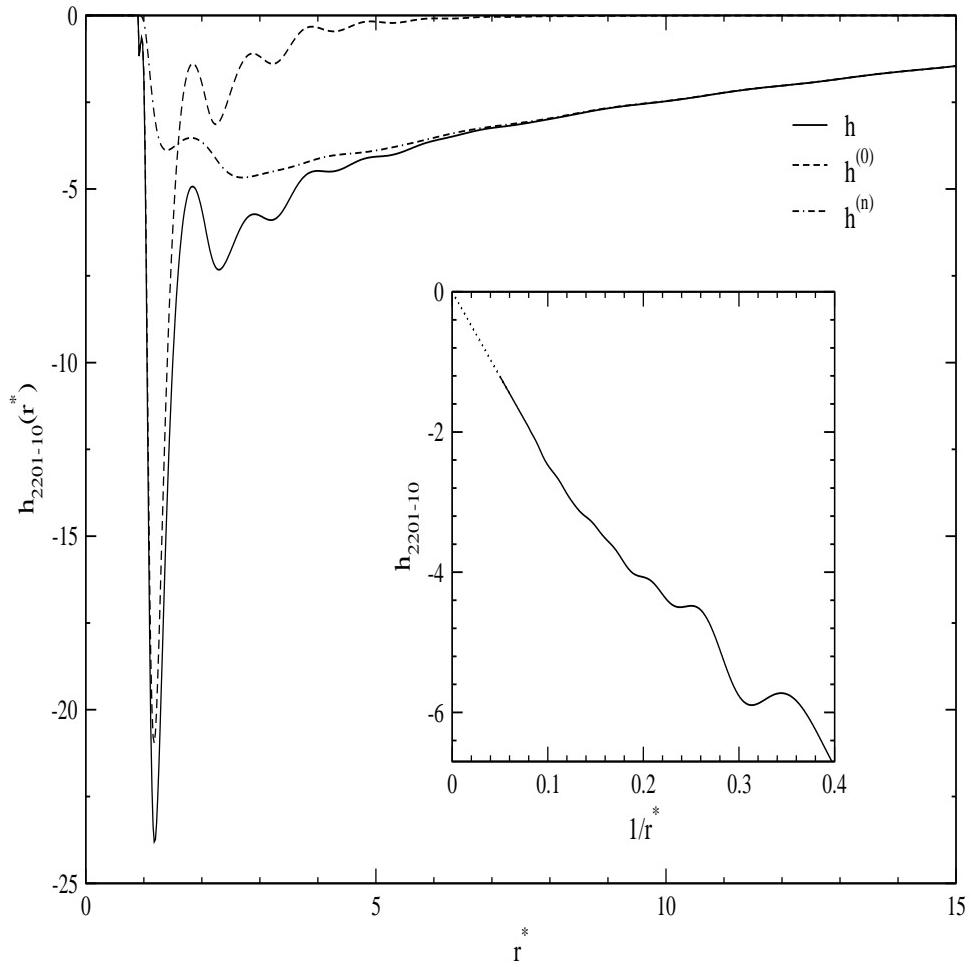


FIG. 4: harmonic coefficient $h_{2201-10}$ in the director frame at $\rho^* = 0.3361$, $T^* = 1.0$ and $P_2 = 0.44$. Details are same as in Fig 1. Inset shows the plot of $h_{2201-10}$ harmonics with respect to $1/r^*$, the dotted line shows the extrapolated part.